Depolarization scattering of light near the critical point

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We have investigated experimentally depolarized scattering of light by mixtures as a result of dipole reradiation. We have observed that it increases strongly near the critical point. We have studied the dependence of the intensity of the scattered light of varying polarization on the distance to the beam.

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The depolarization scattering of light near the critical point has recently been under intensive study.[1–3] Thus, in[1,2] it was predicted that a new strongly-increasing component is present in the spectrum in this region. In addition, measurements of the degree of polarization were used in attempts to estimate the contribution of multiple scattering to the polarization component when determining the critical exponents (see e.g., [4]).

The purpose of the present study was to verify by experiment the physical premises on which[1,2] are based. To explain the specifics of the experiment, we shall briefly describe the theoretical premises that lead to the results of[1,2].

Depolarized scattering of light is due to mutual influence of particles in the course of scattering, and its spectral intensity in the pair approximation[5] is

$$I_{(2)} \sim \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 e^{ik\mathbf{e}_i(\mathbf{r}_1-\mathbf{r}_2)-ik\mathbf{e}_s(\mathbf{r}_3-\mathbf{r}_4)} \cdot T(\mathbf{r}_1-\mathbf{r}_3)T^*(\mathbf{r}_2-\mathbf{r}_4) < \delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2, t)\delta n(\mathbf{r}_3)\delta n(\mathbf{r}_4, t) >_\omega, \quad (1)$$

where $k\mathbf{e}_i$ and $k\mathbf{e}_s$ are the wave vectors of the incident and scattered waves, and $n(\mathbf{r})$ is the density of the number of particles. In the tensor T, which takes into account the initial influence of the particles, a decisive role is assumed in the critical region by the part that acts at the largest distance and is connected with the dipole reradiation. In the four-particle correlator it is also necessary to take into account the long-range nonconnected part, i.e., the correlator must be replaced by a product of paired correlators. We are interested in a binary mixture, for which we assume diffusion kinetics. Then the spectral intensity of the scattering at the angle $\theta=\pi/2$ is

$$I^{l}_{m(2)} \sim \left(\frac{\partial\epsilon}{\partial c}\right)^4_{p,T} \sum_{\mathbf{k}_1} \left(|T^{lm}_{\mathbf{e}_i\mathbf{k}+\mathbf{k}_1}|^2 + T^{lm}_{\mathbf{e}_i\mathbf{k}+\mathbf{k}_1} T^{lm}_{\mathbf{e}_s\mathbf{k}-\mathbf{k}_1} \right) \times < |c_{\mathbf{k}_1}|^2 > < |c_{\mathbf{k}_1} - k(\mathbf{e}_s-\mathbf{e}_i)|^2 > \frac{Dk_1^2 + D|\mathbf{k}_1 - k(\mathbf{e}_i-\mathbf{e}_s)|^2}{\omega^2 + [Dk_1^2 + D|\mathbf{k}_1 - k(\mathbf{e}_i-\mathbf{e}_s)|^2]^2}, \quad (2)$$

where $D(k_1)$ is the diffusion coefficient, c is the concentration, l and m are the polarization directions of the incident and scattered light, and $T^{lm} = -4\pi(k_l'k_m' - k'^2\delta_{lm})/(k^2-k'^2)$. We note that if we put $k=0$ in $T(\mathbf{k}')$ (static-dipole field), then the integral intensity obtained from (2) coincides with the result of Andreev[2] and increases like the correlation length κ^{-1}, while the width of the spectrum is of the order of Dk^2.

However, the bulk of the effect is due to the long-range part of T. Then, allowance for the singularities in the first term of (2) at $k' \sim k$ yields for the integral intensity $I^l_m \sim (\partial\epsilon/\partial c)\kappa^{-4}R^4k^4$, where R is the dimension of the system, which corresponds to[1]. The half-width of this contour is of the order of Dk^2. This result is purely an estimate, since the exact answer depends on the geometry of the system. Of greatest interest here is the strong growth of the intensity as $T \to T_c$ and the R^4 dependence on the dimensions of the scattering system.

We have investigated the depolarization scattering of light in a mixture of nitrobenzene and hexane near the critical lamination point ($c_c = 0.41$ molar fractions of $C_6H_5NO_2$; $T_c = 20.45°$). The measurements were performed with spectral apparatus described earlier.[6] The temperature in the cell, into which the chemically pure components of the mixture were distilled in vacuum, was maintained with accuracy 0.02 °C. The measurements were performed at a fixed angle $\theta=\pi/2$. We analyzed the scattered light of three polarizations I^x_z, I^x_x, and I^y_x. In the components I^x_z and I^y_x we have indeed observed narrow contours that increased strongly as $T \to T_c$. They were much narrower than the Rayleigh-line wings (RLW) so that it is possible to separate the two parts of the spectrum. The RLW intensity hardly

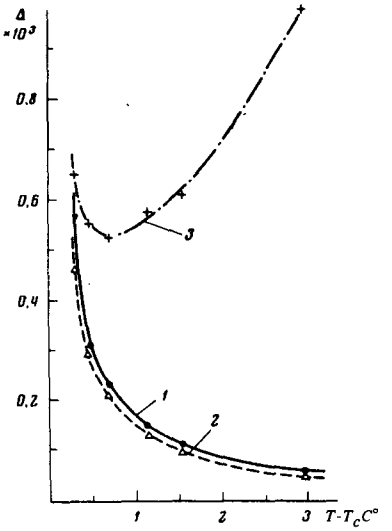

FIG. 1.

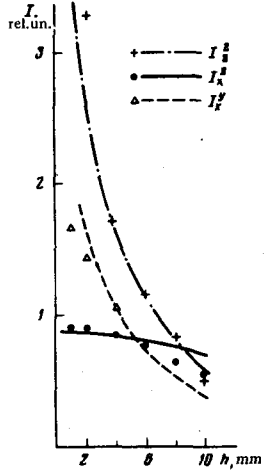

FIG. 2.

changed with temperature. However, the resolving power of the setup ($F \sim 10^7$) was insufficient to determine the rates of the investigated processes. Quantitative measurements of the depolarized components are difficult because of the strong increase of the single scattering $I^z_{z(1)}$. To eliminate it, the components $I^z_{z(2)}$, $I^z_{x(2)}$ and $I^y_{x(2)}$ were measured outside the beam. The experiments revealed no RLW in the measured components. With such an experimental setup, the breakdown of the four-particle correlator in (1) into a product of pair correlators becomes exact.

Figure 1 shows the ratios of the components $I^z_{x(2)}$ and $I^y_{x(2)}$ outside the beam ($h=1$ mm) to I^z_z on the beam as functions of $T-T_c$ (curves 1 and 2). We see in the figure that $I^z_{x(2)}$ and $I^y_{x(2)}$ increase much more rapidly (by approximately $1/(T-T_c)$ times) than I^z_z. Curve 3 shows the degree of depolarization I^z_x/I^z_z against $T-T_c$ on the beam, with allowance for the contribution of the RLW.

Figure 2 shows experimental points that yield the dependence of the components $I^z_{x(2)}$, $I^y_{x(2)}$, and $I^z_{z(2)}$ on the distance to the beam. We do not show here the theoretical curves calculated at a given experimental geometry. Within the limits of the experimental accuracy, the ratio of these curves does not depend on $T-T_c$.

We measured the dependence of the degree of depolarization $\Delta = I^z_x/I^z_z$ at $h=0$ on the diameter d of the laser beam. When d changed by 50 times, Δ changed in proportion. This result is perfectly natural, for by the virtue of the long-range character of the reradiation $I^z_{x(2)}$ depends only on the dimensions of the observed volume, which is shaped like a cylinder whose length always overlaps d. In this case $I^z_{x(2)}$ remains constant, and $I^z_{z(1)}$ decreases in proportion to d.

It thus turns out that the theoretically predicted strong increase of the depolarized component as $T \to T_c$ in the unusual volume dependence actually do take place, and the quantitative agreement between the calculated curves and the experimental ones provide additional corroboration of the validity of the theoretical concepts. It should be noted that the ratio I^z_x/I^y_x depends very strongly on the geometry of the setup, and it appears that the Krishnan effect is entirely due to this fact.[7]

The investigated effect is decisive in depolarized scattering, and also makes an appreciable contribution $I^z_{z(2)}$ to the polarization component. Inasmuch as $I^z_{z(2)} \gg I^z_{x(2)}$ outside the beam (Fig. 2), the estimate of the secondary scattering obtained from the measurement of Δ during the course of determination of the critical exponents is doubtful. On the other hand, it becomes possible here to determine these exponents independently, and also to take a more correct account of the multiple scattering.

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[1]D.W. Oxtoby and V.M. Gelbart, J. Chem. Phys. 60, 3359 (1974).
[2]A.F. Andreev, ZhETF Pis. Red. 19, 713 (1974) [JETP Lett. 19, 368 (1974)].
[3]A.K. Atakhodzhaev, L.M. Kushaev, L.M. Sabirov, V.S. Starunov, T.M. Utarova, and I.L. Fabelinskiĭ, ZhETF Pis. Red. 17, 95 (1973) [JETP Lett. 17, 65 (1973)].
[4]M.A. Anisimov, A.M. Evtyushenkov, F.Yu. Kiyachenko, and I.K. Yudin, ZhETF Pis. Red. 20, 378 (1974) [JETP Lett. 20, 170 (1974)].
[5]A.D. Backingam and M.J. Stephan, Proc. Farad. Soc. 53, 884 (1957).
[6]L.A. Zubkov, N.B. Rozhdestvenskaya, and V.P. Romanov, Zh. Eksp. Teor. Fiz. 65, 1782 (1973) [Sov. Phys.-JETP 38, 891 (1974)].
[7]M.V. Vol'kenshteĭn, Molekulyarnaya optika (Molecular Optics), Moscow (1951).

Erratum: Depolarization scattering of light near the critical point [JETP Lett. 22, No. 1, 5–6 (5 July 1975)]

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In line 13 of the left-hand column, replace $I^{y}_{x(2)}$ by $\frac{1}{2}I^{y}_{x(2)}$. In Fig. 2 on page 6, I^{z}_{z} should be replaced with $\frac{1}{5}I^{z}_{z}$.

